

NOBLE METAL CATALYSTS FOR LOW-TEMPERATURE NAPHTHALENE HYDROGENATION IN THE PRESENCE OF BENZOTHIOPHENE

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INTRODUCTION

The hydrogenation of aromatic and polyaromatic compounds are typically exothermic [1,2]; therefore, a lower reaction temperature is thermodynamically favorable. However, in considering the hydrotreating process of heavy liquids where polycyclic aromatic compounds are abundant, a reaction temperature above 623K is typical which consequently requires a high concentration of hydrogen to offset the limitation of thermodynamic equilibrium conversion. Noble metal catalysts are active for the hydrogenation of aromatics even at a temperature below 473K [2-4], but they were not used for hydrotreating purpose owing to the cost and their susceptibility to the poisoning by sulfur-containing compounds [5]. However, recent studies showed that noble metal catalysts may not be as sensitive to sulfur as what has been recognized [6-10]. This study is therefore attempted to probe the possibility of using noble metal catalysts for low-temperature hydrotreating reaction in the presence of sulfur-containing compounds, and the model reaction of naphthalene hydrogenation in the presence of benzothiophene was used.

EXPERIMENTAL

Pt/Al₂O₃, Pd/Al₂O₃, and Pd/TiO₂ catalysts were all prepared by incipient wetness method using H₂PtCl₆ (Aldrich, 99.995%) and PdCl₂ (Aldrich, 99.995%, dissolved in ultra pure HCl before use) as the precursors. The pore volume and surface area of the support are 0.8 cc/g and 200 m²/g for γ-Al₂O₃ (Sumitomo Metal Mining, S-1, grounded to 80-120 mesh size before use) and 0.5 cc/g and 50 m²/g for TiO₂ (Degussa, P25). The supports were calcined at 773K under dried air flow for 2 h before catalyst preparation. A nominal loading of 2% metal was used for all three catalysts. A commercially available NiMo/Al₂O₃ hydrotreating catalyst (Shokubai Kasei, P-modified and presulfided) was used without further pretreatment and as a reference for comparison in this study. Pretreatment of catalysts were carried out in a flow-type glass reactor which has a side arm to connect to a catalyst transfer tube with which the reduced catalyst powders can be poured into the transfer tube without exposing to the air. The transfer tube loaded with pretreated catalyst was usually stored under N₂ environment in a home-made glove box. The pretreatment conditions for these noble metal catalysts were H₂ reduction at 723K for Pt/Al₂O₃, 20% O₂ calcination at 673K for Pd/Al₂O₃, and H₂ reduction at 473K for Pd/TiO₂; these conditions were found to cause relatively higher activities for naphthalene hydrogenation at 553K with these three noble metal catalysts.

Hydrogenation was studied using tubing bombs made from weld connectors (Swagelok[®], ss316), and a 1/4" tube as the side arm for connection to a pressure gauge and a close-off valve. The total inner volume of the bomb was approximately 25 cc. Bombs were typically loaded with 4 g tridecane (Aldrich, 99%), 1 g naphthalene (Fischer, certified grade), and benzothiophene (Fluka, 99%) in some cases, transferred into the home-made glove box, loaded with pretreated noble metal catalyst, capped using wrenches, transferred out of glove box, and further tightened. Thereafter, the bomb was connected to a gas manifold via its side-arm and the atmosphere inside the bomb was replaced by hydrogen (MG Ind., 99.999%) using dilution purge, i.e., at least 8 cycles of pressurizing with H₂ to 1000 psig followed by a careful venting to approximately 50 psig. At the completion of dilution purge, the bomb was charged with H₂ to either 1000 psig or 1500 psig, disconnected from the manifold, sunk into a fluidized sandbath (Tecam) preset to the desired reaction temperature, and the reaction was timed. After the reaction time was reached, the bomb was removed from the sandbath and quenched in water. The reaction temperature was typically controlled to an accuracy of ±10°C.

After reaction, the pressure in the tubing bomb was carefully released to prevent from any entrainment of liquid in the vent gas; part of the vent gas was collected in a gas bag for later composition analysis. The bomb was then opened and the liquid content was poured into a funnel with filter paper, and the bomb was rinsed and flushed with acetone (Aldrich, 99.9%); the filtrate and the wash solution are separately stored in small vials for later analysis. The solid residue on the filter paper was dried in an oven at 120°C for at least 3 h and then weighed.

The composition of vent gas was analyzed with GC (Perkin-Elmer 5800) using Chemipack C18 (Alltech, 1/8", 6ft) column with FID and Carboxene 1000 (Supelco, 1/8", 15ft) column with TCD. The gas yield and the amount of H₂ reacted were calculated from the average molecular weight of vent gas, the bomb pressure after reaction, and the weight change before and after the bomb was vented. Liquid samples were quantitized by adding known amount of n-nonane (Aldrich, 99.9%) followed by GC (HP5890II) analyses with either a DB-17 (J&W, 30m x 0.25mm) or a Rtx-50 (Restek, 30m x 0.25mm) capillary column and the FID; the response factors of individual species were determined by injection of mixtures of known composition. GC-MS (HP5890II GC with HP5971A MSD) equipped with the same capillary column was used to obtain structural information of unknown species from time to time. The sum of the liquid products in both the filtrate and the wash solution samples were used as the overall yields of liquid products. The yield of solid product was taken as the weight difference between the solid residue and the catalyst loaded in the reactor. An overall mass balance of $\pm 10\%$ was obtained with this kind of analysis; most experiments show an overall mass balance within $\pm 5\%$.

RESULTS AND DISCUSSION

The results of naphthalene hydrogenation at 553K over these three noble catalysts and the NiMo/Al₂O₃ catalyst are shown in Table 1. The naphthalene conversions over Pt/Al₂O₃, Pd/Al₂O₃, and Pd/TiO₂ were all above 70% in the one-hour run, comparing to a 17% conversion over NiMo/Al₂O₃ at a 50% higher catalyst loading; it is clear that the three noble metal catalysts are much more active than the NiMo/Al₂O₃ hydrotreating catalyst at this reaction condition. Also included in Table 1 are the hydrogenation results of TiO₂ and HCl treated Al₂O₃; it is clear that the high activities of these three noble metal catalysts cannot be attributed to the support or the Cl⁻ residue in the catalysts. Beside the higher naphthalene conversions with the three noble metal catalysts, the selectivities to hydrogenated naphthalene products (dihydronaphthalene, tetralin, and decalins) and the ratios of the moles of hydrogen reacted to that of naphthalene reacted, $\Delta H/\Delta N$, are also significantly higher than the NiMo/Al₂O₃ catalyst. The calculated $\Delta H/\Delta N$ ratio for the three noble metal catalysts roughly agrees with the amount of hydrogen added to form the hydrogenated products based on the product analysis. This indicates that the hydrogen reacted was almost all used for hydrogenation with the noble metal catalysts; whereas, for NiMo/Al₂O₃ part of the hydrogen reacted was used to form gas products. This implication agrees with the low yields to solid and gas products with the noble metal catalysts. It is clear that the noble metal catalysts are more suitable for the hydrogenation of naphthalene and, likely, more suitable for the hydrotreating purposes at 553K.

It is interesting to note that the main product of the naphthalene hydrogenation is tetralin at 553K even when the naphthalene conversion is above 90% (Table 1). As the naphthalene hydrogenation and the tetralin hydrogenation are both exothermic reactions, a higher equilibrium yield to deeper hydrogenated products is expected from thermodynamics when a lower reaction temperature is used. Therefore, the naphthalene hydrogenation at 473K was studied and the results are shown in Table 2 for the three noble metal catalysts. It appears that the selectivities to decalins increase only when high naphthalene conversion was achieved at 473K; it seems that a more detailed study is needed if a high selectivity to decalins is desired. However, the hydrogenation abilities of these noble metal catalysts are clearly shown from the high selectivities to hydrogenated products, high $\Delta H/\Delta N$ ratios, and the low selectivities to gases and solids in Table 2. This indicates that noble metal catalysts can be useful for low-temperature polyaromatic hydrogenation.

The results of naphthalene hydrogenation in the presence of benzothiophene are also included in Table 2. The addition of 0.2% (wt) of sulfur in the form of benzothiophene caused a 87, 53, and 39% decrease in the naphthalene conversion respectively for the Pt/Al₂O₃, Pd/Al₂O₃, and Pd/TiO₂ catalysts in the one-hour runs; whereas, a 90, 84, and 57% decrease was observed respectively when 0.5% (wt) of sulfur was added. It is clear that organic sulfur compounds can significantly hinder the hydrogenation activities of noble metal catalysts and a higher sulfur content resulted in a lower conversion during the same period of reaction. However, the above percentages of decrease in naphthalene conversion indicate that palladium catalysts are less sensitive to sulfur compound than the platinum catalyst and that the TiO₂ support can be beneficial in regards to the catalytic hydrogenation activity in the presence of benzothiophene.

Experiments with an extended reaction period (8 h) showed that the naphthalene hydrogenation in the presence of benzothiophene can proceed to a conversion as high as 89 and 78% respectively for Pd/TiO₂ and Pd/Al₂O₃. As no benzothiophene was identified in the liquid products from all the runs with the addition of benzothiophene, it implies that benzothiophene was adsorbed favorably to naphthalene and reacted slower than the naphthalene under the reaction conditions of this study. As the benzothiophene was gradually converted to another sulfur species not held

on the catalytic surface, the naphthalene hydrogenation started and gradually went to completion. Since no other form of sulfur compound was identified in the liquid products except small amount of dihydrobenzothiophene and since the yield to ethylbenzene which is included in R-(1-ring) category in Table 2 increased with the reaction time, it is speculated that the conversion of the benzothiophene over these noble metal catalysts proceeds via a hydrodesulfurization reaction to ethylbenzene and hydrogen sulfide with dihydrobenzothiophene as the intermediate. Accordingly, the hydrogen sulfide formed should not be a poison, at least to the palladium catalysts used in this study. It should be noted that hydrogen sulfide was not included in the products because it could not be identified with the analytical tools used in this study. Although the possibility of the formation of SO₂ species over TiO₂ [6] could not be excluded from this study, the above speculation is preferred because Pd/Al₂O₃ also catalyzed the naphthalene hydrogenation to 78% conversion in the 8-h run with the addition of benzothiophene. It is also interesting to note that the selectivities to hydrogenated naphthalene products were not significantly affected by the presence of benzothiophene, as shown in Figure 1; this again agrees with the speculation that naphthalene hydrogenation could occur simultaneously with the benzothiophene hydrodesulfurization. These results suggest that noble metal catalysts can be useful for low-temperature hydrotreating purpose even when the feed contains sulfur.

In an effort to obtain a quantitative analysis of the effect of benzothiophene on the naphthalene hydrogenation over these noble metal catalysts, a pseudo-first order kinetics [1] is assumed applicable to the results of this study. As a consequence, the apparent rate constants can be estimated by the slopes from a graph like Figure 2, where the results reported for the naphthalene hydrogenation at 553K (Table 1) and the hydrogenation at 473K in the presence of 0.5% (wt) sulfur (Table 2) are presented according to the pseudo-first order kinetics. The effect of sulfur compound on the rate of naphthalene hydrogenation is then estimated by the ratio of the apparent rate constant in the presence of benzothiophene to that with no addition of benzothiophene, i.e., k_s/k . After correcting for the amounts of catalysts used in different runs, the $k_s(473K)/k(553K)$ ratio was found to be 0.1, 0.12, and 0.02 for Pd/TiO₂, Pd/Al₂O₃, and Pt/Al₂O₃ respectively. If the activation energy that Nieuwstad *et al.* reported for 2-methylnaphthalene hydrogenation over Pd/C catalyst [4], 10 kcal/mol, is used to correct for the effect of reaction temperature, then the $k_s(473K)/k(473K)$ ratio becomes 0.46, 0.56, and 0.1 respectively for Pd/TiO₂, Pd/Al₂O₃, and Pt/Al₂O₃. This again indicates that the palladium catalysts are less affected by the presence of benzothiophene. The ratios for the two palladium catalysts are comparable to the calculated k_s/k ratio of 0.73 for NiMo/Al₂O₃ at 623K based on the equation reported by Lo [1,11] and the benzothiophene concentration used in this study. This indicates that the palladium catalysts are comparable to NiMo/Al₂O₃ for simultaneous hydrogenation and hydrodesulfurization even at a lower reaction temperature where NiMo/Al₂O₃ catalyst shows little activity.

From Tables 1 and 2, the three noble metal catalysts studied showed their potentials for applications in the polyaromatic hydrogenation and hydrotreating purposes. The high activities of group VIII metal catalysts toward hydrogenation of alkylbenzenes and of polycyclic aromatic compounds have been known for some times [2-4]; their activities toward hydrogenation of polyaromatic compounds can be orders of magnitude higher than the conventional hydrotreating catalysts such as NiMo/Al₂O₃[2]. Even the presulfided Pt and Pd catalysts showed significantly higher hydrogenation activities and C-N hydrogenolysis activities than sulfided Mo catalyst [12]; this indicates that sulfur-poisoned noble metal catalysts might still have comparable activities to the conventional hydrotreating catalysts. Thus, as the energy efficiency and the activity of the hydrotreating catalyst are concerned, the use of noble metal catalysts for lower-temperature hydrotreating purposes seems to be a reasonable choice. However, the preparation of optimal supported noble metal catalyst for these applications still waits for more detailed studies.

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Table I. Naphthalene Hydrogenation over Various Catalysts at 553K using Tridecane as the Solvent

	NiMo/Al ₂ O ₃	Pt/Al ₂ O ₃	Pd/Al ₂ O ₃	Pd/TiO ₂	TiO ₂	HCl/Al ₂ O ₃
Feed						
Catalyst(mg)	207	127	136	132	137	144
H ₂ ¹ (psig)	1000	1000	1000	1000	1000	1000
N ² (mg)	1001	1001	1003	1002	1011	1002
Reaction						
T ³ (°C)	280	280	280	280	280	280
Time (h)	1	1	2	1	2	1
x _N ⁴ (%)	17	72	86	77	90	84
ΔH ₂ ⁵ (mmol)	2	10	15	10	16	12
ΔH ₂ /ΔN ⁶	1.5	1.8	2.2	1.7	2.2	1.8
Yield ⁷ (mg)	122	804	949	829	992	863
Product (wt%)						
di-H-N ⁸	0.2	0	0	0	0	0
Tetralin	55	92	85	90	90	92
t-Decalin	0	3	7	2	2	1
c-Decalin	0	2	5	0.7	0.4	0.2
R-(1-ring) ⁹	6	0.6	0.6	2	0.5	0.6
R-(2-ring) ¹⁰	1	0.1	0.2	0.1	0.1	0.2
R-(3 ⁺ ring) ¹¹	0	0	0	0	0	0
Solid	0	0.2	0.5	0.3	0.2	0
Gas	38	3	1	5	7	6

¹ H₂ feed at room temperature to an accuracy of ±20 psig.

² Naphthalene.

³ Temperature setting of the sandbath; the accuracy of actual reading is ±10°C.

⁴ Naphthalene conversion, calculated from the amount of N remained and the amount of N fed.

⁵ Number of moles of H₂ reacted.

⁶ Molar ratio of H₂ reacted to N reacted.

⁷ Overall yield of products listed below.

⁸ Dihydronaphthalene.

⁹ R-(1-ring) includes alkylbenzenes and alkylcycloparaffins.

¹⁰ R-(2-ring) includes indenes, indanes, alkyltetralins, alkylindaphthalenes, and biphenyls.

¹¹ R-(3⁺ring) includes species having at least 3-ring structures.

Table 21. Naphthalene Hydrogenation over Pd/Al₂O₃, Pd/Al₂O₃, and Pd/TiO₂ Catalysts at 473K using Tridecane as the Solvent

Feed	Pd/Al ₂ O ₃					Pd/Al ₂ O ₃					Pd/TiO ₂					
	124	207	191	184	196	135	208	199	195	202	138	214	197	194	191	202
Catalyst(mg)	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500
H ₂ (psig)	1002	1004	1003	1004	1001	1001	1004	1001	1002	1002	1002	1002	1001	1000	1001	1001
BT ^a (mg)	0	0	9	21	21	0	0	9	21	21	0	0	21	21	21	21
Reaction	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
T (°C)	2	2	2	2	8	2	2	2	2	8	2	2	2	2	2	8
Time (h)	11	100	13	10	10	42	100	47	16	78	37	100	61	43	61	89
x _N (%)	4	34	3	2	6	8	29	9	4	10	8	33	7	7	11	17
ΔH ₂ (mmol)	4.8	4.3	2.9	2.6	7.7	2.5	3.7	2.4	3.2	1.6	2.8	4.2	1.5	2.1	2.3	2.4
Yield (mg)	115	1072	149	120	133	434	1060	500	187	828	388	1068	636	462	656	949
Product (wt%)																
di-H-N	0	0	0	0	0	0	0	0	0	0	0	0	0.1	0	0	0
Tetralin	44	1	63	20	47	82	36	83	62	93	84	0.5	88	81	89	89
t-Decalin	0	44	0	0	0	0	43	0.5	0	0.3	0.4	76	0.4	0.3	0.2	0.8
c-Decalin	0	49	0	0	0	0	17	0	0	0	0.1	18	0	0.1	0	0.1
R-(1-ring)	3	0	0.2	7	9	1	0	0.8	4	2	2	0	0.8	2	2	1
R-(2-ring)	2	0	0.1	3	1	0.5	0.1	0.1	2	0.3	0.4	0.1	0.2	0.4	0.4	3
R-(3-ring)	0	0	0	0	0	0	0	0	0.4	0	2	0	0.1	0	0	0
di-H-BT ^b	0	0	0	1	0	0	0	0.2	5	0.1	0	0	0	0.8	0.2	0
Solid	6	1	1	11	0	1	0.2	0	0	0.1	0	0	0	0.1	0.1	0.5
Gas	46	6	35	59	43	16	5	15	28	5	12	5	10	15	9	6

¹ See footnotes of Table 1.

² Benzothiophene.

³ Dihydrobenzothiophene.

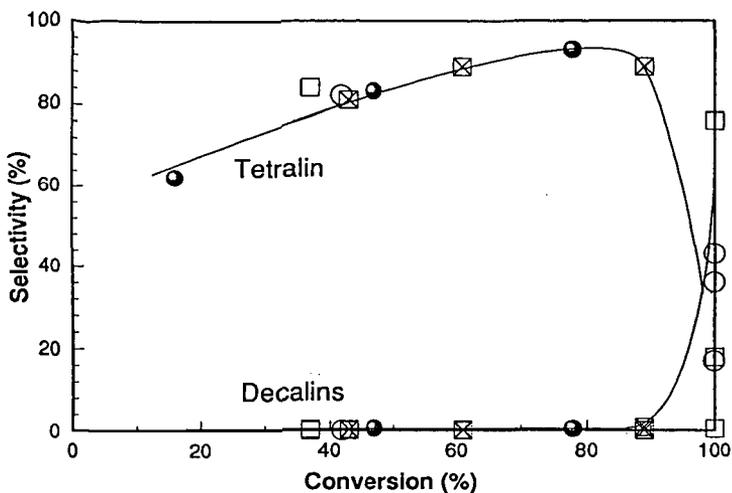


Figure 1. Selectivity to tetralin and decalins as a function of naphthalene conversion during the naphthalene hydrogenation at 473K over Pd/Al₂O₃ (○, ●) and Pd/TiO₂ (□, ⊠). Open symbols: runs with no addition of benzothiophene; filled symbols: runs with the addition of benzothiophene.

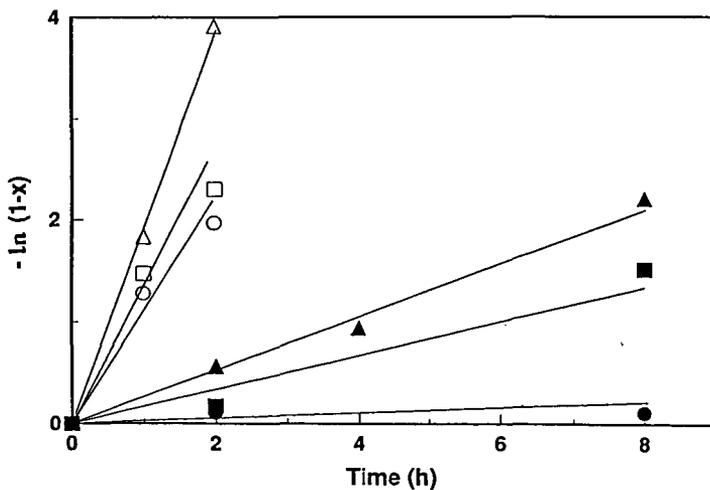


Figure 2. Pseudo-first-order plot of the naphthalene hydrogenation over Pt/Al₂O₃ (○, ●), Pd/Al₂O₃ (□, ■) and Pd/TiO₂ (△, ▲). Open symbols: runs at 553K with no addition of benzothiophene; filled symbols: runs at 473K with the addition of benzothiophene.